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(54) **Water-absorptive vinyl lactam polymer compositions**

(57) A composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form a hydrogel is made by blending (1) 40 to 98% by weight of water-soluble polymer of an N-vinyl lactam or a copolymer thereof with 1 to 90 mole percent of a copolymerizable monomer containing a polymerizable ethylenic unsaturation

but excluding homopolymers of 1-vinyl-2-pyrrolidone; and (2) 2 to 60% by weight of a water-insoluble copolymer formed of 50% to 90% by weight based on the total copolymer of a hydrophobic water-insoluble ethylenically unsaturated monomer, 2 to 12% by weight of an ethylenically unsaturated monomer containing an acid group, and 15 to 45% by weight of a hydrophilic ethylenically unsaturated monomer free from acidic groups.

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SPECIFICATION

Water-absorptive compositions

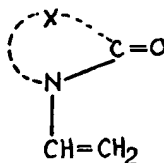
This invention relates to a composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form a hydrogel and pertains more specifically to an optically clear blend of a water-soluble poly(vinyl lactam) or of a water-soluble copolymer of a vinyl lactam with 1 to 90 mole percent of copolymerizable monomer containing a polymerizable ethylenic unsaturation, with a water-insoluble copolymer derived from 50% to 90% by weight, based on the total weight of the copolymer, of a hydrophobic water-insoluble ethylenically unsaturated monomer, 2% to 12% by weight of an ethylenically unsaturated monomer containing an acid group, and 15 to 45% by weight of a hydrophilic ethylenically unsaturated monomer free from acidic groups.

It has previously been proposed to insolubilize polymeric N-vinyl lactams such as poly(vinyl pyrrolidone) by reaction with water-soluble polymers containing carboxyl groups, the reaction product precipitating from solution when the two are mixed, as described in Stoner U.S. Patent 2,901,457. As pointed out by Stoner et al. at column 4, lines 56—73, the reaction product there described always has substantially the same properties and contains the two polymeric components in the same proportions regardless of the proportions of the two used to make the product. The compositions of the present invention, on the other hand, vary in properties and in proportions of components depending upon proportions of starting materials. It has also been proposed in O'Driscoll et al. U.S. Patent 3,700,761, in Gruzca U.S. Patent 3,807,398, and in Le Boeuf et al. U.S. Patent 4,018,853 to make covalently cross-linked hydrogels by polymerizing hydrophilic methacrylate monomers in the presence of poly(vinyl pyrrolidone). Moreover, it has been reported in Boyer-Kawonoki, Compt. Rend., Ser. C, Vol. 263, p. 278 (Chem. Abs. Vol. 65, 20283d) 1966 that an I.R. spectrum of the addition product of poly(vinyl Pyrrolidone) and poly(acrylic acid) indicated hydrogen bonding between the pyrrolidone carbonyl groups and the carboxyl groups of the poly(acrylic acid). In Ono et al. U.S. Patent 3,975,570, it has been proposed to improve the moisture permeability of conventional pressure-sensitive adhesives which are copolymers of alkyl acrylates with acrylic or methacrylic acid by blending with them hydroxyethyl cellulose, and it was stated that blends of such adhesives with poly(vinyl pyrrolidone) did not exhibit improved moisture permeability. Other blends of a poly(vinyl lactam) with various copolymers are described and claimed in copending applications of Shah Serial No. 137,297 filed April 4, 1980 and of Shah and Temin Serial No. 142,986 filed April 23, 1980.

The compositions of the present invention are capable of absorbing more than 45% of their own weight of water when immersed in water at room temperature and may absorb even more than ten times their weight of water. Despite the absorption of such large amounts of water, the compositions retain their coherence and dimensional integrity and do not dissolve; these characteristics make them particularly useful for several bio-medical purposes which require that the hydrogel come into intimate contact with body tissue or cavities.

The mechanism of interaction between the water-soluble vinyl lactam polymer or copolymer and the water-insoluble copolymer in the blend is not fully understood, but the blend does behave like a physical mixture rather than a chemical reaction product in that it can be separated into the two polymeric components by gel permeation chromatography. The blends are optically clear and substantially free from haziness, indicating that the blend is homogeneous despite the fact that the vinyl lactam polymer or copolymer is water-soluble and the copolymer is water-insoluble. Examination at high magnification under an electron microscope shows the presence of microphase domains (4000 Å or less in diameter) of water-insoluble material dispersed in the continuous phase of water-soluble vinyl lactam polymer or copolymer. The presence of these microphase domains of the water-insoluble copolymer prevents dissolution of the continuous phase polymer in water, but unlike covalent cross-linking of polymers does not render the blend non-thermoplastic. Instead, the blend possesses the ability to be repeatedly shaped or formed under moderate pressure at a temperature as low as 150°C., or in some cases even lower. The shaped or formed composition retains its shape at room temperature subject to distortion when swollen with water. The compositions of the present invention in which the dispersed submicroscopic particles (micro-phase domains) act as multiple cross-links to prevent dissolution of the hydrophilic continuous phase (which by itself is water-soluble), form a new class of hydrogels, distinct from those in which the cross-linking is provided by weak cohesive forces, hydrogen bonds, ionic bonds, or covalent bonds.

The vinyl lactams, polymers and copolymers of which can be used in the present invention, are preferably N-vinyl lactams including those having the structure



in which X represents an alkylene bridge having three to five carbon atoms, such as 1-vinyl-2-pyrrolidone, 1-vinyl-5-methyl-2-pyrrolidone, 1-vinyl-2-piperidone, and N-vinyl-ε-caprolactam, homopolymers of 1-vinyl-2-pyrrolidone being excluded. The polymers and copolymers may also be formed from various N-vinyl oxazolidinones including N-vinyl oxazolidinone itself and various 4- and/or 5-alkyl substituted N-vinyl oxazolidinones. The copolymerizable monomers with which the N-vinyl lactams can be copolymerized to form copolymers containing 10 to 99, preferably 25 to 99, mole percent N-vinyl lactam and correspondingly 1 to 90, preferably 1 to 75, mole percent of comonomer, include N,N-dimethyl acrylamide, glyceryl methacrylate, diethylene or triethylene glycol monomethacrylate or other hydrophilic monomers, as well as vinyl acetate, alkyl acrylate or methacrylate, vinyl alkyl ethers, acrylonitrile, vinyl chloride, or other hydrophobic monomers. In the case of monomers such as vinyl acetate which themselves form water-insoluble homopolymers, the upper limit of the amount of such monomer which can be employed to form the desired water-soluble copolymer is much lower than in the case of monomers such as N,N-dimethyl acrylamide which form water-soluble homopolymers. These polymers and copolymers may have molecular weights from 10,000 to 1,000,000 or more, but those having molecular weights to 1,000,000 are preferred. Copolymers of 1-vinyl-2-pyrrolidone are preferred.

The water-insoluble copolymers which can be employed as blends with the vinyl lactam polymer or copolymer in the compositions of the present invention include water-insoluble copolymers of a hydrophobic water-insoluble ethylenically unsaturated monomer such as alkyl esters of acrylic or methacrylic acid in which the alkyl group has from 1 to 16 carbon atoms, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl chloride, vinylidene chloride, ethylene, propylene, butylene butadiene and other polymerizable alkenes, vinyl alkyl ethers and vinyl alkyl ketones in which the alkyl group has 3 or more carbon atoms. The copolymers also include as another essential monomer an ethylenically unsaturated monomer containing an acid group such as a carboxylic, sulfonic, or phosphonic acid group; among suitable acidic monomers are acrylic acid, methacrylic acid, crotonic acid, maleic acid, 2-sulfoethyl methacrylate and 1-phenyl vinyl phosphonic acid. The third monomer is selected from a group of hydrophilic ethylenically unsaturated monomers possessing a solubility parameter in excess of 11 [calories/cm³]^{1/2}, free from acidic groups, such as methacrylamide, acrylamide, *p*-styrene sulfonamide, hydroxyethyl methacrylate, diethylene glycol monomethacrylate, triethylene glycol monomethacrylate and glyceryl methacrylate.

In the case of each of the three types of monomers a mixture of two or more individual monomers of the same type can be used.

Compatibility or incompatibility of the water-insoluble copolymer with the water-soluble vinyl lactam polymer or copolymer in the hydrated form of the blend, that is, its suitability for use in the present invention, can in each case be readily determined by visual examination of a blend of the two polymers after equilibration in water at room temperature. If the blend is transparent and optically clear and remains so after immersion in water at 20°C. without dissolution in the water, it forms a satisfactory hydrogel. If the blend is cloudy or opaque after equilibration in water, or if it dissolves in water at 20°C., the blend made from that copolymer is not satisfactory and possesses poor mechanical properties. For a blend composition to possess satisfactory mechanical properties in the hydrated form, the size of the microphase domains of the terpolymer in the hydrogel should not be greater than 4,000 Å, and preferably should be below about 1000 Å.

The relative proportions of the different monomers in the water-insoluble copolymer may vary widely; the hydrophobic water-insoluble ethylenically unsaturated monomer may amount to 50% to 90% by weight, based on the total weight of the copolymer, while the ethylenically unsaturated monomer containing an acidic group may amount to 2% to 12% by weight; the hydrophilic ethylenically unsaturated monomer may amount to 15 to 45% by weight. The exact proportions of the three types of monomers are determined by the hydrophobic-hydrophilic balance required in each case.

Thus, in the case of one preferred class of water-insoluble copolymers the amount of methyl methacrylate (or styrene or 2-ethylhexyl acrylate) is from 55 to 70% by weight based on the total copolymer weight, the amount of acrylic acid is from 2 to 12% by weight, and the amount of methacrylamide is from 25—43% by weight.

In the case of another preferred water-insoluble copolymer, the amount of *n*-butyl methacrylate is from 55 to 80% by weight based on the total copolymer weight, the amount of acrylic acid is from 2 to 12% by weight, and the amount of methacrylamide is from 15 to 35% by weight.

In the case of still another preferred water-insoluble copolymer, the amount of *n*-butyl methacrylate is from 50 to 78% by weight of the total copolymer, the amount of acrylic acid is from 2 to 12% by weight, and the amount of hydrophilic *p*-styrene sulfonamide is from 20 to 35% by weight. In another preferred water-insoluble copolymer, the amount of *n*-butyl methacrylate is from 55 to 70% of the total copolymer weight, acrylic acid is from 2 to 12%, and hydroxyethyl methacrylate is from 25 to 43%.

The relative proportions of water-soluble vinyl lactam polymer or copolymer and of water-insoluble copolymer in the blend vary over a wide range, from 40 to 98% by weight, preferably from 50 to 98%, based on the total weight of the blend, of the former and from 2 to 60% by weight, preferably from 2 to 50%, of the water-insoluble copolymer; optimum proportions of each within the range vary

depending upon the particular properties desired in the blend as well as upon the identity of the particular polymer or copolymer present in the blend. The greater the proportion of the water-insoluble copolymer in the blend, the lower is the equilibrium water content of the resultant hydrogel. The water content of the blend hydrogels of this invention can be varied from approximately 30% to 95% or higher by judicious selection of the water-soluble and water-insoluble polymer and copolymer and its proportion in the blend. In general, the higher the water content of the hydrogel, the poorer becomes its mechanical properties.

The blend can be made by mixing together solutions or dispersions of the water-soluble polymer or copolymer and of the water-insoluble copolymer in any desired vehicles or solvents which are miscible with each other, then removing the vehicle or solvent, as by evaporation. It may also be possible to blend the two components on a hot roll mill or in an extruder or in other conventional mixing equipment. Shaped articles of the blend can be prepared by casting from a suitable solvent or by a molding process under the influence of heat and pressure.

The thermoplasticity of these hydrogel-forming blends confers on them a special processing advantage over covalently cross-linked synthetic hydrogels. Tailoring of mechanical and physical properties (e.g., water content, solute and water permeability, softness, flexibility and tensile strength) of the hydrogel is readily accomplished by control of the physico-chemical characteristics and the proportion in the blend of the water-insoluble copolymer. In addition, the physical properties of the blend can be modified by the inclusion of a compatible, water-soluble suitable solvent. The coating has a good adhesion to glass, is colorless, optically clear, and non-fogging upon exposure to hot, moist air.

The following specific examples are intended to illustrate more fully the nature of the present invention without acting as limitations upon its scope.

EXAMPLES 1—8

A series of water-soluble 1-vinyl-2-pyrrolidone copolymers containing varying proportions of vinyl acetate, N,N-dimethylacrylamide, and mixtures of both of the latter two was prepared by dissolving the desired proportions of monomers in equal volumes of methanol and by employing as initiator approximately 0.15% by weight (based on monomers) of a free radical generator such as 2,2'-azobisisobutyronitrile. Polymerization was carried out under solvent reflux conditions to a degree of conversion of about 90—95%, and the copolymer was obtained as a residual brittle transparent and colorless solid after evaporation of solvent and residual monomers by heating the reaction mix at 100°C. under vacuum.

A water-insoluble copolymer of a mixture of 62 parts by weight of n-butyl methacrylate, 30 parts of methacrylamide, and 8 parts of acrylic acid was prepared by a conventional solution polymerization procedure by dissolving the desired proportions of monomers in a 1 : 1 by weight mixture of ethyl alcohol and dioxane and by employing as an initiator of polymerization a small amount (0.2—0.4% by weight of monomers) of a free radical generator such as azobisisobutyronitrile or 2-t-butylazo-2-cyanopropane. Polymerization was carried out at 80—95°C. to a high degree of conversion. The copolymer was isolated from the reaction mixture by precipitation into methanol, collected by filtration, and dried at 100°C. under a vacuum.

Blends of the water-soluble and water-insoluble copolymers were prepared by dissolving the copolymers in the desired proportions in N,N-dimethylformamide to obtain a solution containing 10—15% by weight of the polymeric blend and subsequently evaporating the solvent at 100°C in vacuo, leaving a mass of optically transparent blended solid material. Approximately 8—12 mil thick sheets of the blends were compression molded, after which they were equilibrated in deionized water at room temperature for 72 hours.

The compositions of the vinyl pyrrolidone copolymers, the amounts of the copolymers in blends with the water-insoluble copolymer, and the equilibrium water content of each hydrogel blend in deionized water at room temperature after 72 hours are set forth in the following Table I. In each case the blends were optically transparent solids, forming optically transparent hydrogels when equilibrated in water.

TABLE I

Example No.	Water-Soluble Copolymer Mole Ratio			Blend Parts by Weight of Water-Soluble Copolymer per 100 Parts of Blend	Equilibrium Water Content Weight %
	DMA	VP	VA		
1	—	50	50	90	70
2	—	50	50	70	59
3	90	10	—	90	77
4	90	10	—	70	65
5	70	30	—	90	79
6	70	30	—	70	67
7	50	25	25	90	76
8	50	25	25	70	65

DMA — N,N-Dimethylacrylamide

VP — N-Vinyl Pyrrolidone

VA — Vinyl Acetate

EXAMPLE 9

Poly-E-caprolactam (Peak M.W. 36,000) was prepared as follows:

- 200 mg. of azobisisobutyronitrile (AIBN) were dissolved in 100g. of N-vinyl-E-caprolactam which
 5 had been previously heated to 45°C in a beaker. The solution was kept in an oven at 75°C for 4 hours, by which time the composition had polymerized to a solid mass. The solid was dissolved in one liter of chlorform and the solution added dropwise to ten liters of petroleum ether (B.P. range 30°C—60°C) with agitation to obtain a granular precipitate of polymer; the polymer was isolated by filtration and dried in a vacuum over (50°C—3 hours at 100 mm Hg). The yield was 75 g. of polymer whose gel
 10 permeation chromatographic peak M.W. was 36,000. The infra-red spectrum showed absorption at 1640 cm⁻¹, characteristic of lactam carbonyl. 10

EXAMPLES 10—13

- Each of the copolymers of these Examples was prepared by conventional solution polymerization procedure by dissolving the desired proportions of monomers in a suitable solvent, the compositions of
 15 the polymerization mixtures being shown in Table II, and by employing as an initiator of polymerization a small amount (0.2—0.4% by weight of monomers) of a free radical generator such as azobisisobutyronitrile or 2-*t*-butylazo-2-cyanopropane. Polymerization was carried out at 80—95°C to a high degree of conversion. Copolymers of the Examples 10 to 12 were isolated from the reaction mixture by precipitation into methanol, collected by filtration, and dried at 100°C under vacuum,
 20 whereas the colymer of Example 13 was isolated by removal of the volatiles by heating in vacuum at 100°C. 20

TABLE II

Reaction Ingredients	Example No.			
	10	11	12	13
Comonomers — Grams				
Methyl methacrylate	65	—	—	—
Methacrylamide	30	30	15	30
Styrene	—	65	—	—
Acrylic acid	5	5	5	5
<i>n</i> -Butyl methacrylate	—	—	80	—
2-Acrylamido-2-methyl- propane sulfonic acid	—	—	—	—
2-Ethylhexyl acrylate	—	—	—	65
Solvents — Milliliters				
Ethanol	100	100	100	100
Dioxane	100	100	100	—
N,N-Dimethylformamide	—	—	—	100

EXAMPLES 14—20

Each of the blend compositions of these Examples was prepared by dissolving in N,N-dimethylformamide the desired proportions of the water-insoluble copolymer and the poly-E-caprolactam as prepared in Example 9 to obtain a solution containing 10—15% by weight of the polymeric blend. The solution of the blend was then heated at 100°C under a vacuum to evaporate the solvent, leaving a mass of optically transparent blended solid material. The blend, which was thermoplastic, was pressed into a disc in a mold heated at 150°C. The molded disc was placed in deionized water for 72 hours, during which time it absorbed water and swelled to form a hydrogel. The compositions of the blends, their physical appearance, and the equilibrium water content of their hydrogels are described in Table III.

TABLE III

Example No.	BLEND OF COMPOSITION		PHYSICAL APPEARANCE		Equilibrium Water Content Weight %
	Copolymer of Example No.	Parts by Weight of poly-E-caprolactam per 100 parts of the Blend	Dry Form	Hydrated Form	
14	10	70	Transparent, solid	Transparent, strong	68
15	10	90	"	"	91
16	11	70	"	"	58
17	11	90	"	"	80
18	12	90	"	Translucent, coherent	70
19	13	70	"	Transparent, strong	77
20	13	90	"	"	90

EXAMPLE 21

Examples 14 to 20 were repeated using a higher molecular weight polyvinyl caprolactam (Peak M.W. 8,000,000). This polyactam was prepared by solution polymerization in methanol. Thus a solution of 100g. of N-vinyl-E-caprolactam in 550 ml of methanol was dissolved 100mg. of azobisisobutyronitrile as initiator. The solution was stirred for 20 hours at 50°C while under nitrogen in a resin kettle equipped with a reflux condenser. The polymer solution was dried in a vacuum oven at 50°C and 10 mm pressure. The peak M.W. was 500,000.

The results were similar to Examples 14 to 20.

10 EXAMPLE 22

Examples 14 to 20 were again repeated using a poly-N-vinyl-E-caprolactam prepared in water similarly to the polymer preparation of Example 22, but using water in place of methanol and 1.2g of potassium persulfate and 0.6g of solution metabisulfate in place of AIBN. The temperature-time sequence was 50°C for 3 hours and then 60°C for 17 hours (rather than 50°C for 20 hours). The peak molecular weight was 600,000.

EXAMPLE 23

Examples 14 to 20 were again repeated using in lieu of the polyvinyl caprolactam, the following polymers:

- (a) polyvinyl 2-piperidone (H.W. — 250,000)
- (b) polyvinyl -5-methyl-pyrrolidone (H.W. — 360,000)
- (c) polyvinyl oxazolidinone (H.W. — 40,000)
- (d) polyvinyl oxazolidinone (H.W. — 350,000).
- (e) polyvinyl-5-ethyl-oxazolidinone (H.W. — 340,000)

The results were similar to those of Examples 14 to 20.

25 EXAMPLE 24

Hydroxyethyl methacrylate (HEMA) was purified by extracting (4 to 6 times) a 1 : 1 solution of the polymer in water with petroleum ether, then saturating the aqueous monomer solution with sodium chloride, and extracting the monomer with chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate and the solution distilled *in vacuo* (0.1 mm on Hg) using cuprous chloride as inhibitor. The monomer fraction distilled over at 70—82°C.

A copolymer of 52% butyl methacrylate, 40% HEMA and 8% acrylic acid was prepared in the usual way, as described in Examples 10—13, employing 25% concentration of the monomers in a mixture of ethyl alcohol and dioxane.

Optically clear blends of the polymer in varying proportions with each of the polymers of Examples 9, 21, 22 and 23(a) to (e) were prepared as described in Examples 14—20 by dissolving the

copolymer and the polymer in dimethylformamide and subsequently evaporating the solvent at 100°C *in vacuo*. Approximately 8—12 mil thick sheets of the blends were compression molded, after which they were equilibrated in deionized water at room temperature for 72 hours. It was found that blends containing 70, 80 and 90% by weight of the polymer formed hydrogels containing 75.8%, 82.3% and 88.9% by weight of water, respectively.

EXAMPLE 25

A copolymer of 62% butyl methacrylate, 8% acrylic acid, and 30% methacrylamide was prepared by the same general method as described in Examples 10—13, and optically clear blends of the resultant copolymer with amounts of each of the polymers of Examples 9, 21, 22 and 23(a) to (e) of from 60 to 90% by 5% increments were prepared as described in Examples 1—8.

It was found that a linear relationship existed between the proportion (10 to 40%) of the copolymer in the blend and equilibrium water content of the resultant hydrogels.

EXAMPLE 26

Examples 1 to 8 were repeated except that in place of 1-vinyl-2-pyrrolidone used as a component of the copolymer (Examples 1—6) or terpolymer (Examples 7 and 8) there were used:

- (a) N-vinyl-2-piperidone
- (b) N-vinyl-5-methyl-pyrrolidone
- (c) N-vinyl-4-methyl-5-butyl-oxazolidone
- (d) N-vinyl oxalidinone

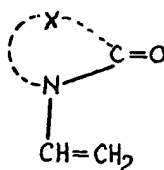
The results are similar to those of the other Examples.

The blends of the present invention possess the properties of thermoplasticity, fusibility, and solubility in organic solvents as well as hydratability. But while they retain the thermoplasticity, fusibility, and solubility in organic solvents of the vinyl lactam polymer or copolymer portion of the blend, they exhibit varying hydration characteristics of that portion depending upon the amount of copolymer present.

CLAIMS

1. A composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form an optically clear hydrogel consisting essentially of an optically clear blend of (1) 40 to 98% by weight, based on the total weight of the blend, of a water-soluble polymer of a vinyl lactam or a water-soluble copolymer thereof with 1 to 90 mole percent of copolymerizable monomer containing a polymerizable ethylenic unsaturation but excluding homopolymers of 1-vinyl-2-pyrrolidone, said polymer or copolymer having a molecular weight of at least 10,000 and (2) 2 to 60% by weight of a water-insoluble copolymer consisting essentially of 50 to 90% by weight, based on the total weight of the copolymer, of a hydrophobic water-insoluble ethylenically unsaturated monomer, 2 to 12% by weight of an ethylenically unsaturated monomer containing an acid group, and from 15 to 45% by weight of a hydrophilic ethylenically unsaturated monomer free from acidic groups.

2. A composition as claimed in Claim 1, in which component (1) is a water-soluble polymer or copolymer of a vinyl lactam having the structure



in which X represents an alkylene bridge having three to five carbon atoms.

3. A composition as claimed in Claim 2, in which component (1) is a water-soluble copolymer of N-vinyl-2-pyrrolidone.

4. A composition as claimed in Claim 1, in which component (1) is a water-soluble polymer of an N-vinyl oxazolidinone.

5. A composition as claimed in any preceding claim, in which said water-insoluble copolymer is derived from 55 to 70% by weight, based on the total weight of the copolymer, of a monomer selected from methyl methacrylate, styrene, and 2-ethylhexyl acrylate, 2 to 12% by weight of acrylic acid, and 25 to 43% by weight of methacrylamide.

6. A composition as claimed in any one of Claims 1 to 4, in which said water-insoluble copolymer is derived from 55 to 80% by weight of n-butyl methacrylate, based on the total weight of the copolymer, 2 to 12% by weight of acrylic acid, and 15 to 35% by weight of methacrylamide.

7. A composition as claimed in any one of Claims 1 to 4, in which said water-insoluble copolymer is derived from 50 to 78% by weight, based on the total weight of the copolymer, of n-butyl

methacrylate, 2 to 12% by weight of acrylic acid, and from 20 to 35% by weight of *p*-styrene sulfonamide.

8. A composition as claimed in any one of Claims 1 to 4, in which said water-insoluble copolymer is derived from 55 to 70% by weight, based on the total weight of the copolymer, of *n*-butyl methacrylate, 2 to 12% by weight of acrylic acid, and from 25 to 43% by weight of hydroxyethyl methacrylate.

9. A composition as claimed in any one of Claims 1 to 8, in which polymer or copolymer (1) has a molecular weight of from 10,000 to 1,000,000.

10. A water-absorptive composition as claimed in Claim 1 and substantially as herein described with reference to any one of Examples 1—8 and 14—26.

11. A catheter or suture coated with a composition as claimed in any preceding claim.

12. A composition as claimed in any one of Claims 1 to 10 having a drug incorporated therein.

13. A glass sheet coated with a composition as claimed in any one of Claims 1 to 10.

14. The features as herein disclosed, or their equivalents, in any novel selection.